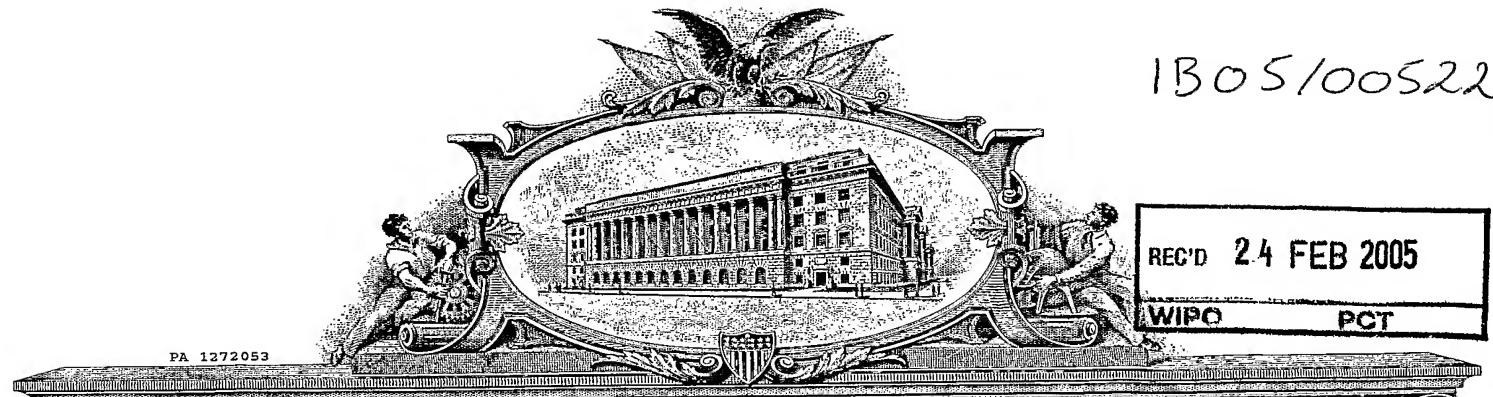


1B05100522



PA 1272053

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

January 14, 2005

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

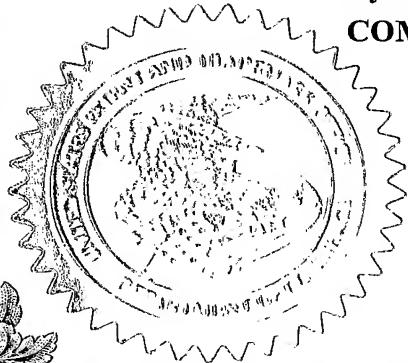
APPLICATION NUMBER: 60/550,908

FILING DATE: March 05, 2004

PRIORITY DOCUMENT

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

EV 388268985 US

22857 U.S.PTO
C655 50908
030504**INVENTOR(S)**

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Ashutosh	Misra	Plano, Texas
Matthew	Fisher	Allen, Texas
Benjamin	Jurcik	Richardson, Texas

 Additional inventors are being named on the _____ separately numbered sheets attached hereto**TITLE OF THE INVENTION (500 characters max)****COMPOSITION AND METHOD FOR DEPOSITION OF HIGH-K DIELECTRIC FILMS**

Direct all correspondence to:

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ENCLOSED APPLICATION PARTS (check all that apply) Specification Number of Pages

27

CD(s), Number

 Drawing(s) Number of Sheets

Other (specify)

 Application Data Sheet. See 37 CFR 1.76**METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT** Applicant claims small entity status. See 37 CFR 1.27.FILING FEE
AMOUNT (\$) A check or money order is enclosed to cover the filing fees The Commissioner is hereby authorized to charge filing
fees or credit any overpayment to Deposit Account Number:

01-1375

\$160.00

 Payment by credit card. Form PTO-2038 is attached.The invention was made by an agency of the United States Government or under a contract with an agency of the
United States Government. No. Yes, the name of the U.S. Government agency and the Government contract number are: _____

Respectfully submitted,

SIGNATURE

Date 03/05/2004

TYPED or PRINTED NAME Linda K. Russell

REGISTRATION NO.
(if appropriate)
Docket Number:

34,918

TELEPHONE 713-624-8956

IDQP 739

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.: Unknown

Applicant: Ashutosh Misra, et al.

Filed: March 5, 2004

TC/ A.U.: Unknown

Examiner: Unknown

Title: COMPOSITION AND METHOD FOR DEPOSITION OF HIGH-K
DIELECTRIC FILMS

Attorney Docket: IDQP 739

CERTIFICATE OF MAILING BY EXPRESS MAIL

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

I hereby certify that the following documents, which are attached, are being deposited, under 37 CFR 1.10, with the United States Postal Service "Express Mail Post Office to Addressee" service as Express Mail No. EV 388268985 US in an envelope addressed to: Box Patent Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on March 5, 2004.

1. Patent application including 27 sheets of specification;
2. Fee Sheet (in duplicate); and
3. Postcard.

Respectfully submitted,



Stacy L. Forte

Date: March 5, 2004
AIR LIQUIDE
2700 Post Oak Boulevard, Suite 1800
Houston, Texas 77056
(713) 624-8957



COMPOSITION AND METHOD FOR DEPOSITION OF HIGH-K DIELECTRIC FILMS

SUMMARY:

This invention relates to a chemical formulation and method for deposition of high-k (high dielectric constant) thin films on substrates.

BRIEF DESCRIPTION:

This invention relates to an improvement in semiconductor manufacturing technology. In the current integrated circuit manufacturing schemes, the transistors employ a thin dielectric between the source and drain regions. As device dimensions shrink, the thickness of this dielectric (also referred to as the gate dielectric) will shrink proportionally, but a very thin gate dielectric will not possess the required reliability due to unacceptable leakage currents. This problem can be solved by replacing the current dielectric with a material of higher dielectric constant. Compounds of hafnium, such as hafnium oxides, hafnium silicates and hafnium silicon oxy nitrides are currently the most promising high-k gate dielectric choices. This invention provides a method and composition for depositing thin high-k dielectric films.

BACKGROUND:

1. Chlorine mobility during annealing in N₂ in ZrO₂ and HfO₂ films grown by atomic layer deposition by Ferrari, S.; Scarel, G.; Wiemer, C.; Fanciulli, M. [Journal of Applied Physics, VOL. 92, NO. 12, 15 Dec. 2002, PP. 7675-7] In this article, it is indicated that any chlorine incorporated in hafnium oxide films is extremely stable, which is an undesirable attribute. In contrast, the present invention uses precursors that are completely chlorine free, thereby avoiding any issues with chlorine inclusion in the film.

2. Method of forming a silicate dielectric layer ; INVENTOR(S)- Jenq, Jason, Jyh-Shyang Ping-Tung City; PATENT APPLICATION NUMBER- 136349/10; DATE FILED- 2002-05-02

This application relates to a method for forming a silicate dielectric layer. The first is to form a silicate layer on the substrate of the wafer by using a physical vapor deposition (PVD) procedure. The silicate layer is a hafnium silicate (HfSi) layer or a zirconium silicate (ZrSi) layer. Then the silicate layer is treated to become a gate dielectric layer or an inter-layer dielectric layer which has higher a dielectric constant by using a rapid thermal annealing (RTA) procedure in a environment which is filled of nitrogen or ammonia. The drawback of this procedure is the use of physical vapor deposition, which does not produce very conformal films.

3. PAJ 02-01-02 02053960 JP CVD RAW MATERIAL COMPOSITION FOR DEPOSITING ZIRCONIUM AND HAFNIUM SILICATE FILM, ITS PRODUCTION METHOD AND METHOD FOR DEPOSITING SILICATE FILM USING THE SAME; INVENTOR(S)- KADOKURA, HIDEKIMI; TAKESHITA, KATSUNORI; PATENT APPLICATION NUMBER- 2000272283; DATE FILED- 2000-08-04;

To provide a metallic alkoxide raw material composition for depositing a zirconium silicate or hafnium silicate film useful as a gate insulating film by a CVD method, further to provide its production method and to provide a film deposition method using the same composition. $Zr(OtBu)_4 + Si(OtBu)_4$ or $Hf(OtBu)_4 + Si(OtBu)_4$ is suitable as a CVD raw material composition since the same is present as one liquid in the vicinity of room temperature, and the vaporizing characteristics and thermal decompositing characteristics of the components are close. The drawbacks of this method are the following – (a) use of liquid silicon source which has to be premixed with the metal (Hf or Zr) source, allowing very little control over the film composition (b) the silicon source has additional carbon in the ligands, which will lead to increased carbon content in the high-k film.

4. PAT 06-04-02 06399208 Source reagent composition and method for chemical vapor deposition formation or ZR/HF silicate gate dielectric thin films; INVENTOR(S)- Baum, Thomas H.; Paw, Witold; PATENT NUMBER- 06399208; PATENT DATE- 2002-06-04

A precursor composition for forming a zirconium and/or hafnium silicate film on a substrate, e.g., by chemical vapor deposition (CVD). Illustrative precursor compositions include (1) a first precursor metal compound or complex including a silicon aloxide (siloxide) ligand coordinated to a metal M, wherein M=Zr or Hf and (2) a second precursor metal compound or complex including an aliphatic aloxide ligand coordinated to a metal M, wherein M=Zr or Hf, wherein the relative proportions of the first and second precursors relative to one another are employed to controllably establish the M/Si ratio in the deposited silicate thin film. The drawback of this method is that while the relative amounts of Si and Hf (or Si and Zr) in the final film are somewhat controllable by the relative amounts of precursor (1) and (2) as noted above, the control is still limited by the actual composition of precursor (1) which contains both the Si and Metal (Hf or Zr).

5. APL 2003-06-19 20030111678/US-A1 CVD deposition of M-SION gate dielectrics; INVENTOR(S)- Colombo, Luigi Visokay, Mark, R. Bevan, Malcolm, J Rotondaro, Antonio, L.P. TX, US; PATENT APPLICATION NUMBER- 184521/10; 341521/60; DATE FILED- 2002-06-28

A method for forming a high-k gate dielectric film (106) by CVD of a M-SiN or M-SION, such as HfSiO. Post deposition anneals are used to adjust the nitrogen concentration. A method for fabricating an integrated circuit, using the steps of: providing a partially fabricated semiconductor body; and forming a gate dielectric by: chemical vapor deposition of a high-k film comprising metal, silicon, and nitrogen a surface of a semiconductor body using a silicon precursor selected from the group consisting of tetrakis(dimethylamido)silicon and tetrakis(diethylamido)silicon, a metal precursor selected from the group consisting of tetrakis(dimethylamido) metal and

tetrakis(diethylamido)metal, where metal is Hf, Zr, La, Y, Gd, Eu, or Pr; and a nitrogen-containing precursor. The drawback of this invention is the use of liquid phase precursors for both the silicon and hafnium source. Liquid phase precursors can lead to formation of residue in the vaporizer and the co-deposition of hafnium and silicon may be affected by difference in the volatilities of the two precursors.

PROBLEM SOLVED:

The novelty of this invention is the use of a volatile silicon precursor which can be used in conjunction with a liquid phase hafnium or zirconium precursor for the deposition of hafnium/zirconium silicon oxy nitride films of desired stoichiometry. In addition to it possessing sufficient vapor pressure at room temperature to allow gas phase delivery, this precursor is also carbon and chlorine free.

SOLUTION OF THE PROBLEM:

This invention discloses a method for depositing films containing X-silicon-oxygen-nitrogen where X is typically Hf or Zr by using a mixture of a source of X (such as Hf(DEA)₄), which is typically in liquid phase and a gas phase mixture of trisilylamine (a carbon and chlorine free silicon source), ammonia (nitrogen source) and nitrous oxide (oxygen source). The liquid phase precursor is injected into a system that vaporizes it into a gas phase, and enters the chamber where the substrate (on which deposition is needed) is placed at an elevated temperature (typically around 400 C). Simultaneously, trisilylamine, nitrous oxide and ammonia are introduced at controlled levels into the chamber. The reaction of various species in the chamber leads to the formation of a hafnium silicon oxynitride film on the heated substrate. The composition of such films can be controlled by varying the flow rates of each of the listed precursors. Because the silicon, oxygen and nitrogen sources in this invention are all carbon and chlorine free, it is possible to deposit a high-k film with excellent properties.

WHAT IS CONSIDERED IMPORTANT:

A silicon source that is carbon and chlorine free and possesses the necessary characteristics required for deposition of a silicon nitride film at temperatures around 600 C.

A silicon source that possesses sufficient vapor pressure at room temperature to allow its delivery in vapor phase through traditional gas flow control systems. This provides significant stoichiometry control during the deposition process, which is not achieved by use of liquid phase silicon sources.

DETAILED DESCRIPTION OF VARIOUS EMBODIMENTS:

1. A composition and method for depositing high-k dielectric films with the composition M-Si-O-N where M is Hf, Zr, La, Y, Gd, Eu, or Pr. The composition includes:
 - a. A silicon source which is:
 - i. free of carbon and chlorine
 - ii. sufficiently volatile to allow vapor phase delivery to process tools
 - b. A nitrogen source which is
 - i. Free of carbon and chlorine
 - ii. sufficiently volatile to allow vapor phase delivery to process tools
 - c. A metal (M) source, where M is Hf, Zr, La, Y, Gd, Eu, or Pr
 - d. An oxygen source which is:
 - i. Free of carbon and chlorine
 - ii. sufficiently volatile to allow vapor phase delivery to process tools

2. Additional features may include one or more of the following:

- a. The silicon source is trisilylamine**
- b. The nitrogen source is ammonia**
- c. The metal source is dialkylamino, alkoxy or inorganic compound of Hf, Zr, La, Y, Gd, Eu, or Pr**
- d. The oxygen source is N₂O, Ozone or Carbon Dioxide**
- e. The deposition process is a chemical vapor deposition (CVD) process at temperatures in the range of 400 – 900 C**
- f. The deposition process is an atomic layer deposition (ALD) process**

3. PowerPoint presentation enclosed.



Selection of Si precursor for Use with Hf(DeA)4

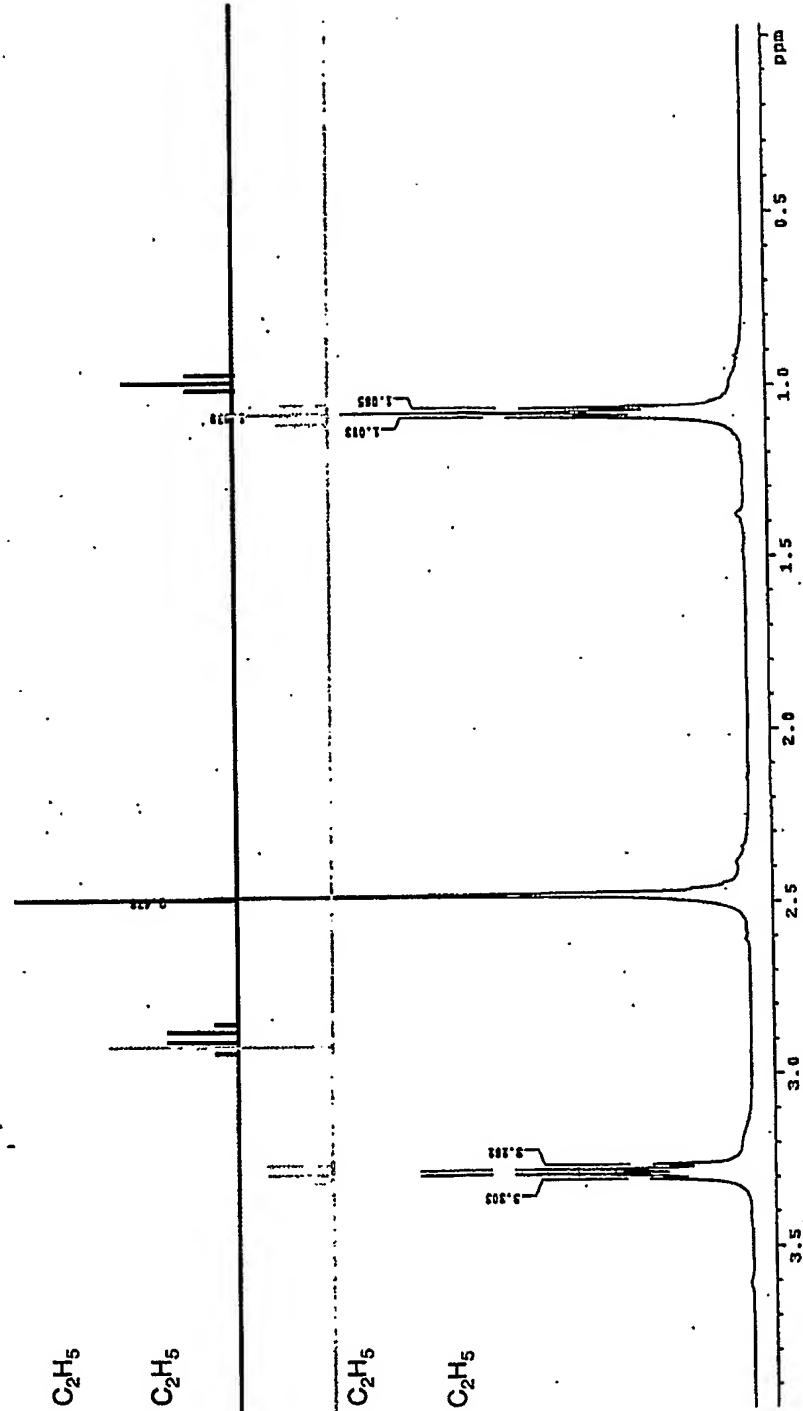
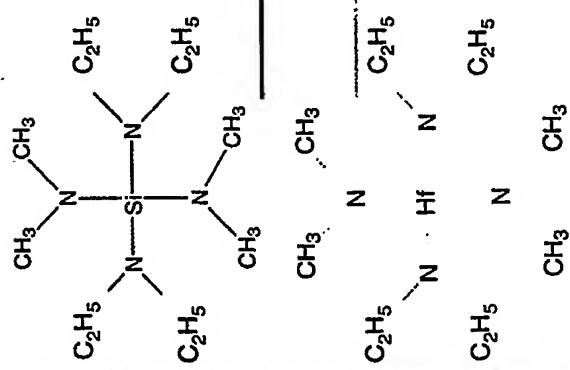
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Possible Choices

1. $\text{Si(NEt}_2\text{)}_4$: Si(DEA)_4
2. $\text{Si(NMe}_2\text{)}_4$: Si(DMA)_4
3. $(\text{SiH}_3)_3\text{N}$: TSA (350 Torr Vap. P)
4. $\text{Si}_2(\text{NHEt})_6$: AHEAD
5. Si(NHEt)_4 : TEAS
6. SiH(DEA)_3 : Tris SiDEA
7. SiH(DMA)_3 : Tris SiDMA
8. Variety of other Si precursors, not yet examined

^1H NMR of $\text{Si}(\text{DMA})_4 + \text{Hf(DEA)}_4$ Mixture

AIR LIQUIDE
Electronica

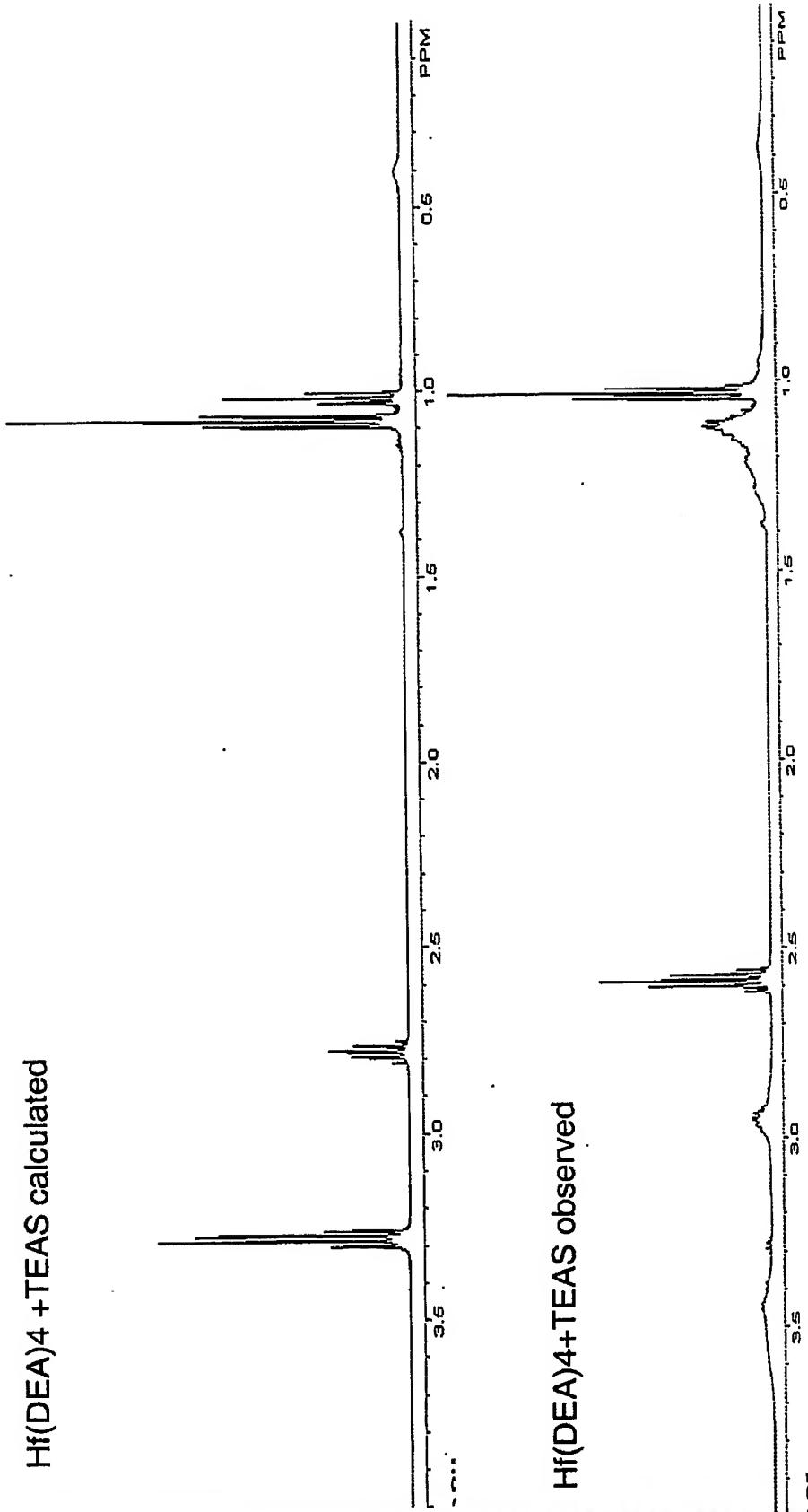


No ligand exchange observed

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Hf(DEA)4 + TEAS Compatibility by ^1H NMR Analysis

Hf(DEA)4 + TEAS calculated



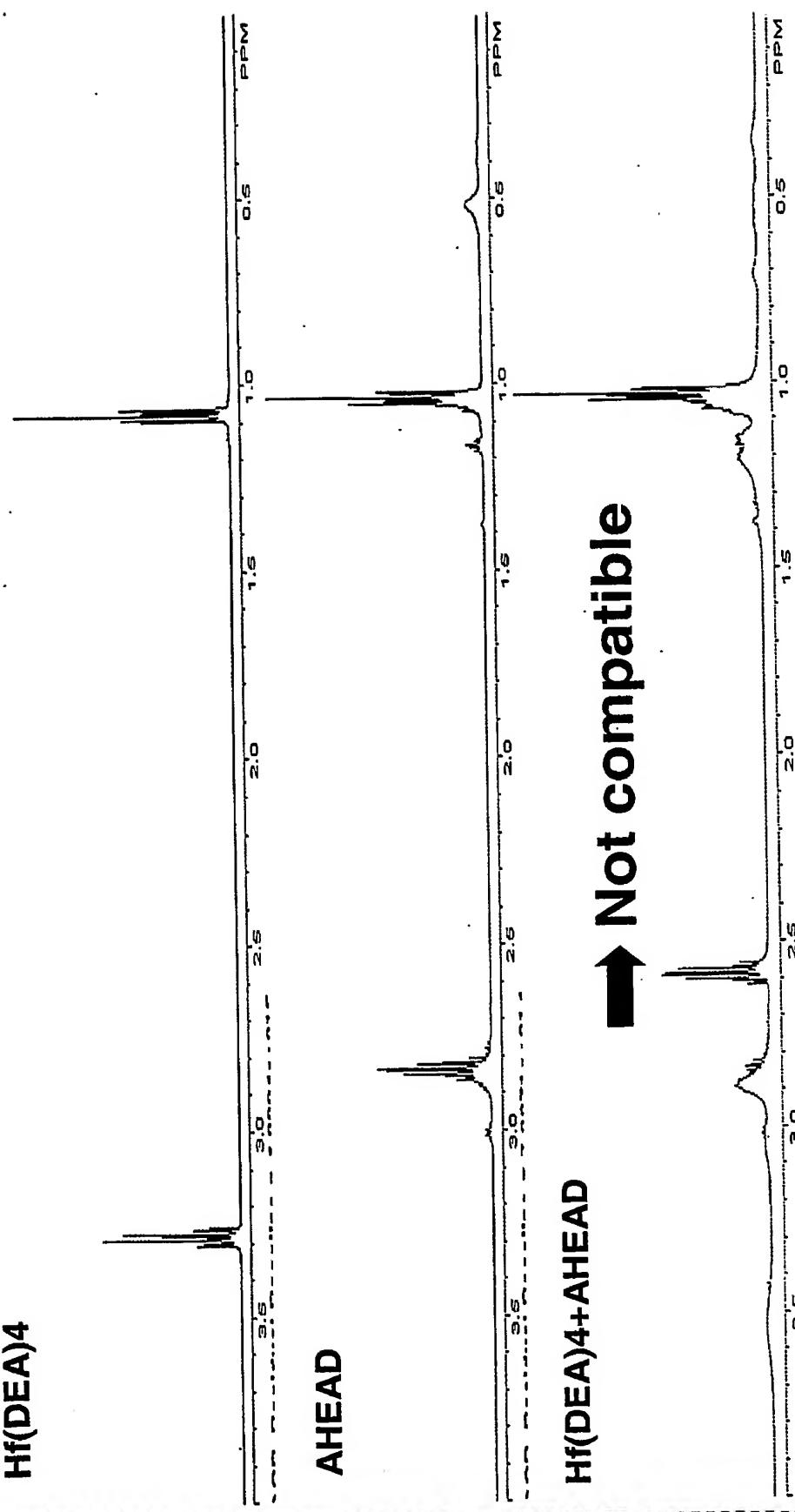
➡ Not compatible

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Hf(DEA)4 + AHEAD Compatibility by ^1H NMR Analysis



Hf(DEA)4



Hf(DEA)4+AHEAD

Not compatible

Summary: monoalkylamino silanes not compatible with Hf(DEA)4

But dialkylamino silanes are.

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Suggested Precursors

Issues with Si(DMA)₄

Si(DMA)₄ has significant levels of Cl impurity as seen in analysis of product from different suppliers

Initial Cl level = 14%

after purification = 0.4% (still significant)

Possible Reason :

Starting material for Si(DMA)₄ synthesis is SiCl₄

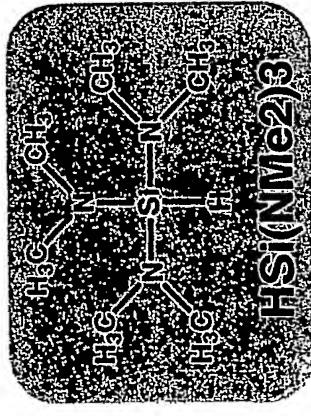
The tris- compounds have Cl levels below detection limit (200 ppm).

Proposed compounds –

1. SiH(DEA)₃
2. SiH(DMA)₃

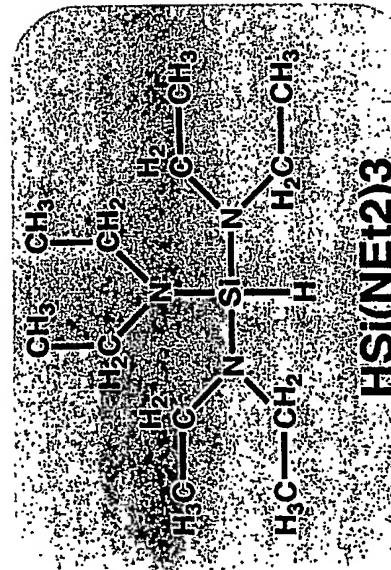
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Tris-Silicon Compounds



HSi(NMe₂)₃

- ✓ Liquid precursor
- ✓ Lower Cl impurity
- ✓ Compatibility with Zr,Hf amino precursors
(same functional group)
- ✓ Possibility to make azeotropic mixture
(with Zr,Hf amino precursors)
- ✓ Possibility of self cleaning property



HSi(NEt₂)₃

- Cl impurity measurement by Ion chromatography*
- ✓ HSi(NMe₂)₃ from Air Liquide
 - ✓ 200 vol ppm (< DL)
 - ✓ Si(DMA)₄ from other supplier
 - ✓ 1: 14% [=Si(NMe₂)₃Cl]
 - ✓ 2: 0.4%

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Specifications for Tris diethylaminosilane

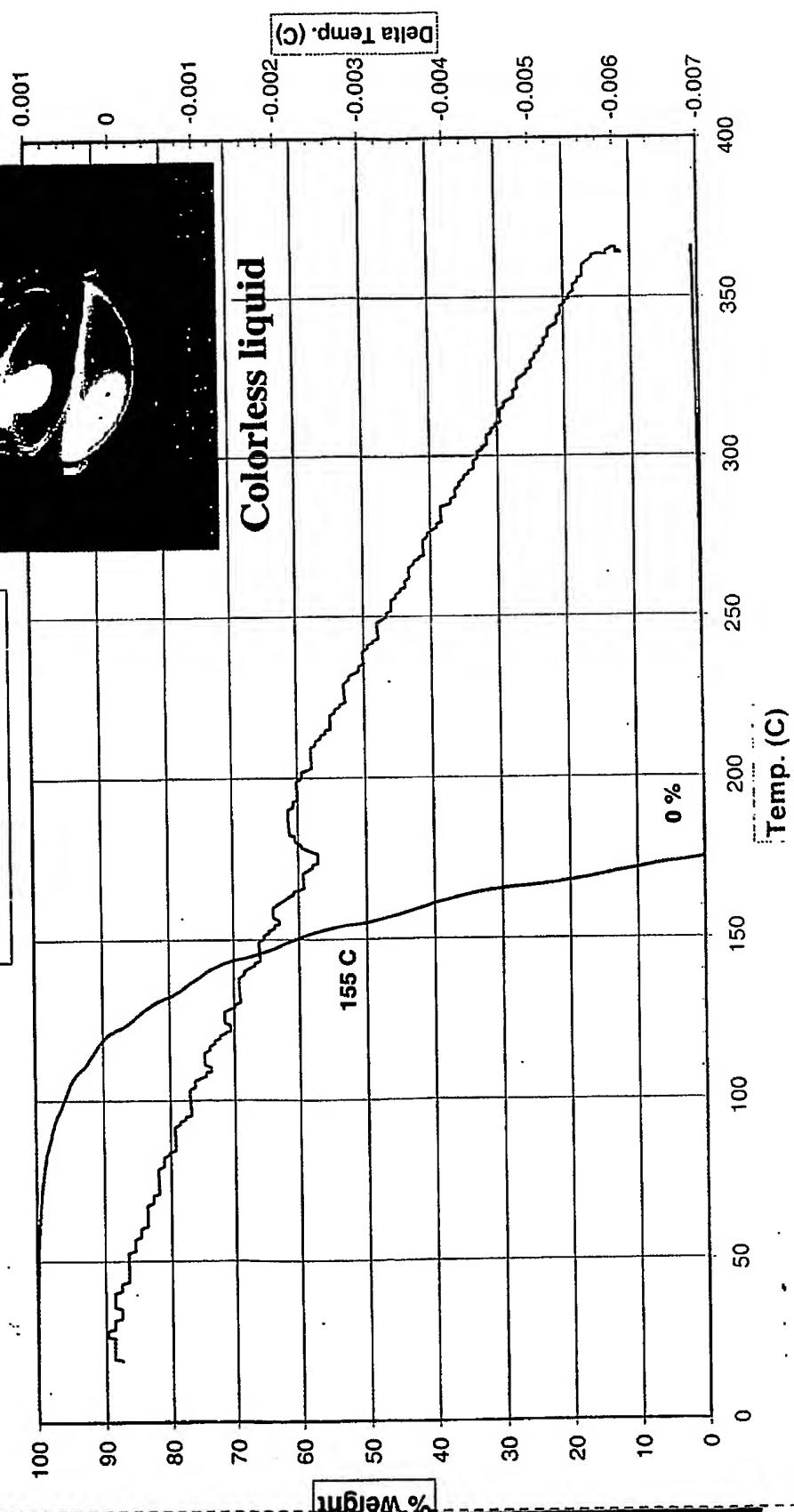


Chemical Name : Trisdiethylaminosilane
Formula : HSi[N(C₂H₅)₂]₃
Purity : 99.9999%

Impurity	Unit	Guaranteed Value
Cr	wt.ppb	50
Co	wt.ppb	50
Fe	wt.ppb	50
Mg	wt.ppb	50
Mn	wt.ppb	50
Na	wt.ppb	50
Ni	wt.ppb	50
Sn	wt.ppb	50
Zn	wt.ppb	50

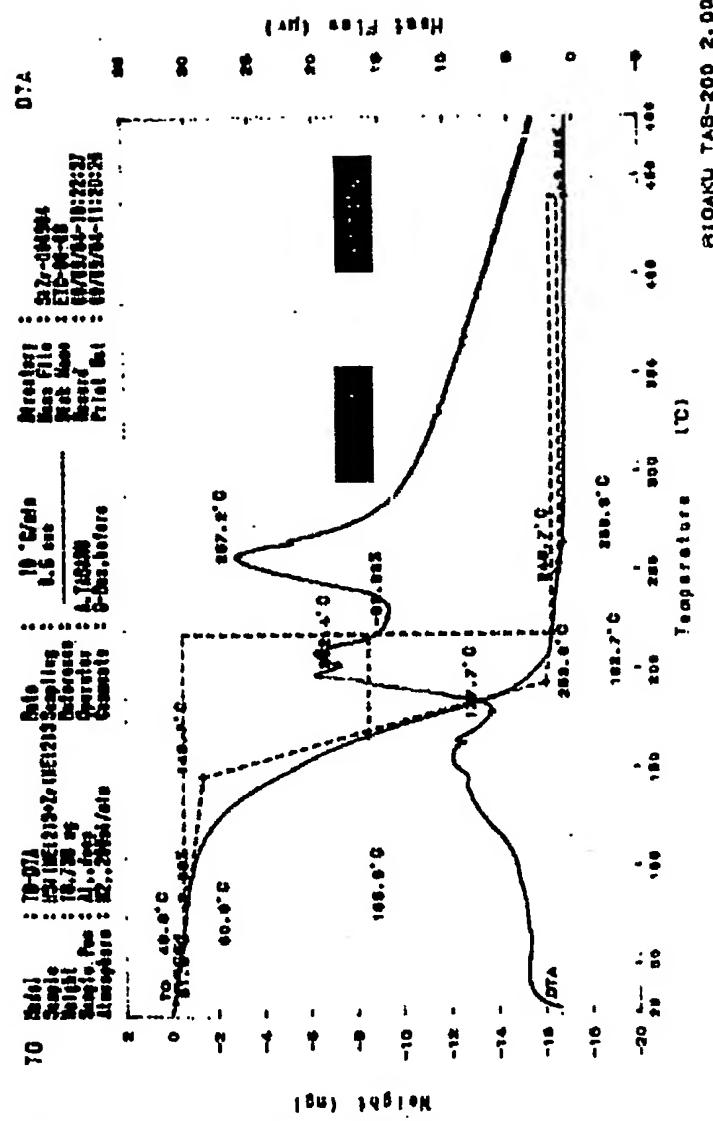
TGA-DTA of HSi(NEt₂)₃

Trisdiethylamino Silane



TGA-DTA of HSi(NEt₂)₃ & Zr(NEt₂)₄

Before heating



Pale yellow liquid

Mixture ratio

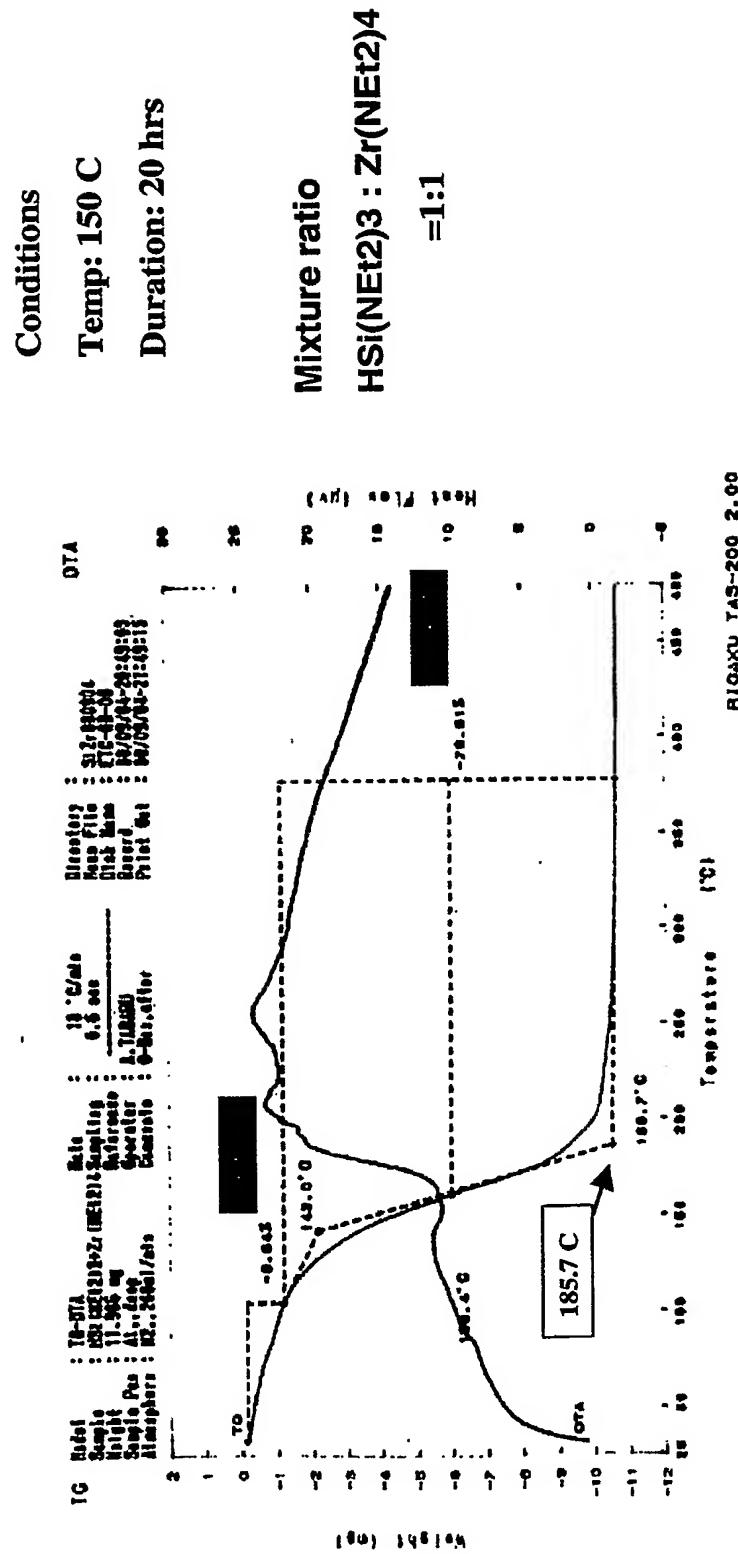
$\text{HSi}(\text{NEt}_2)_3 : \text{Zr}(\text{NEt}_2)_4$

=1:1

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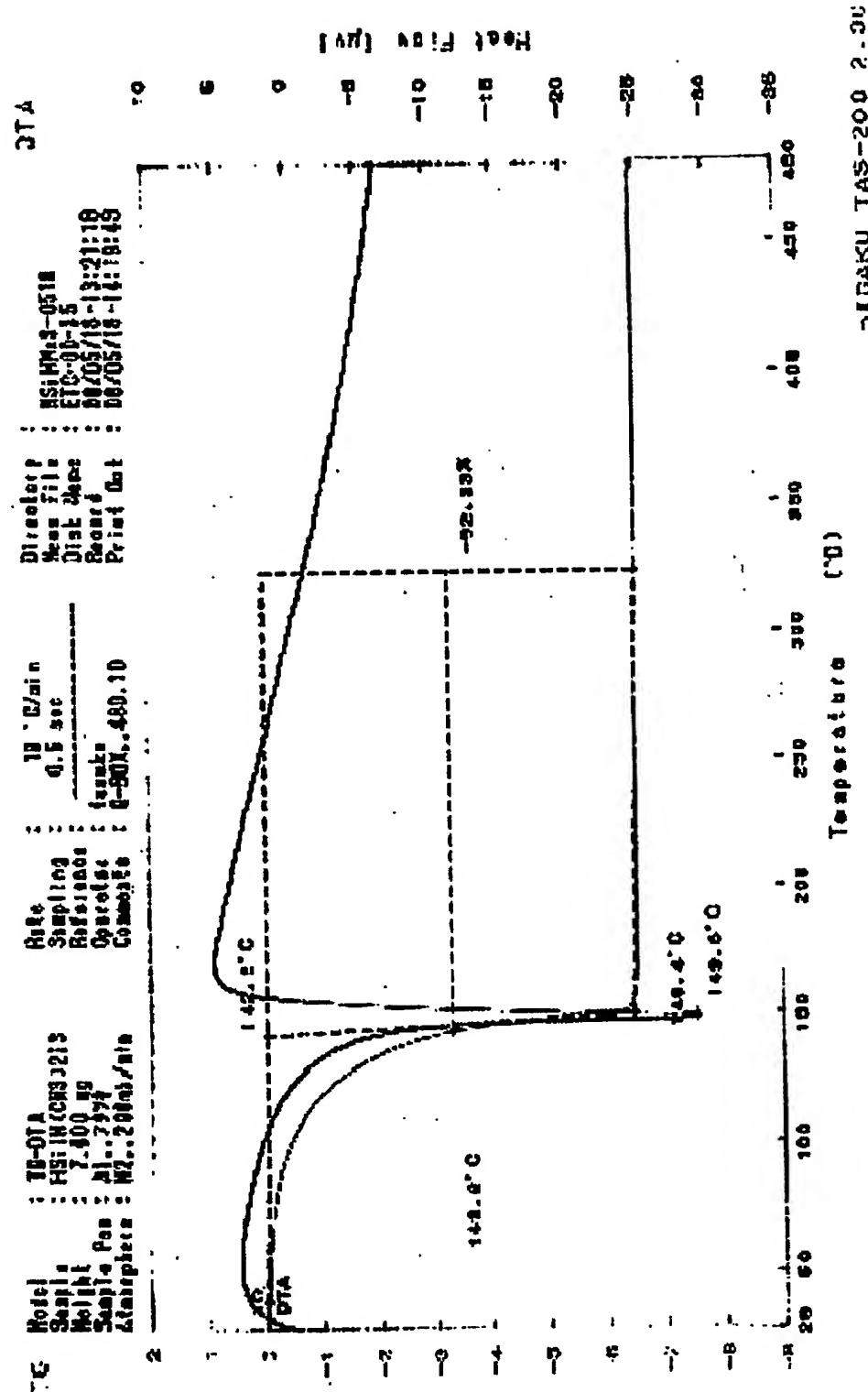
TGA-DTA of HSi(NEt₂)₃ & Zr(NEt₂)₄

After heating



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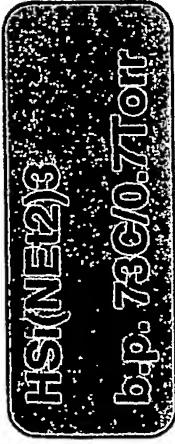
TGA-DTA of HSi(NMe₂)₃



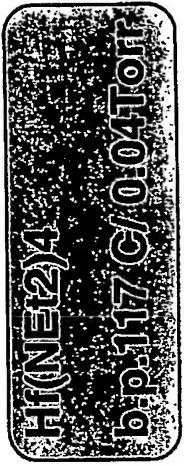
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✓ Si Source



✓ Hf Source

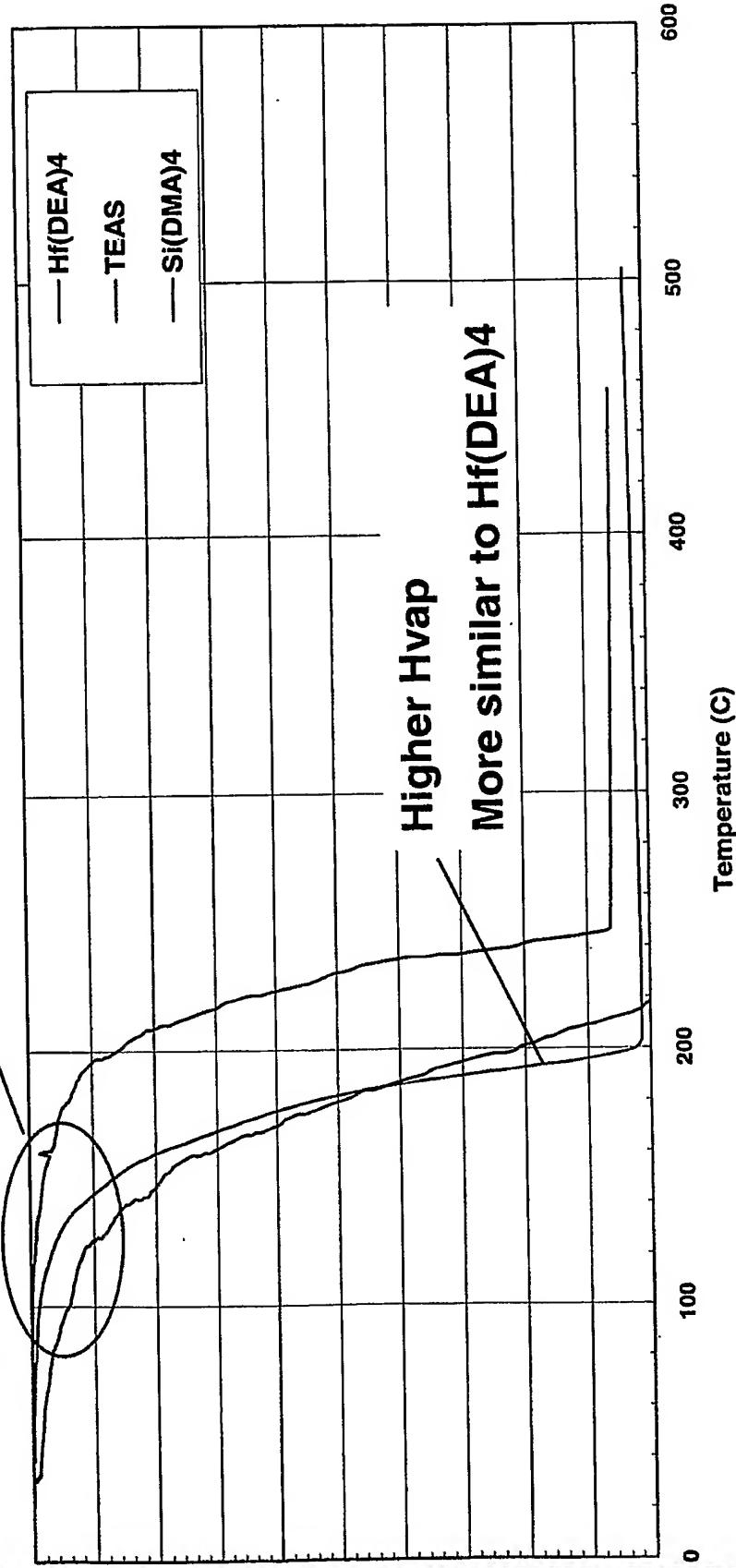


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TGA of Hf and Si Precursors



Vaporization Region

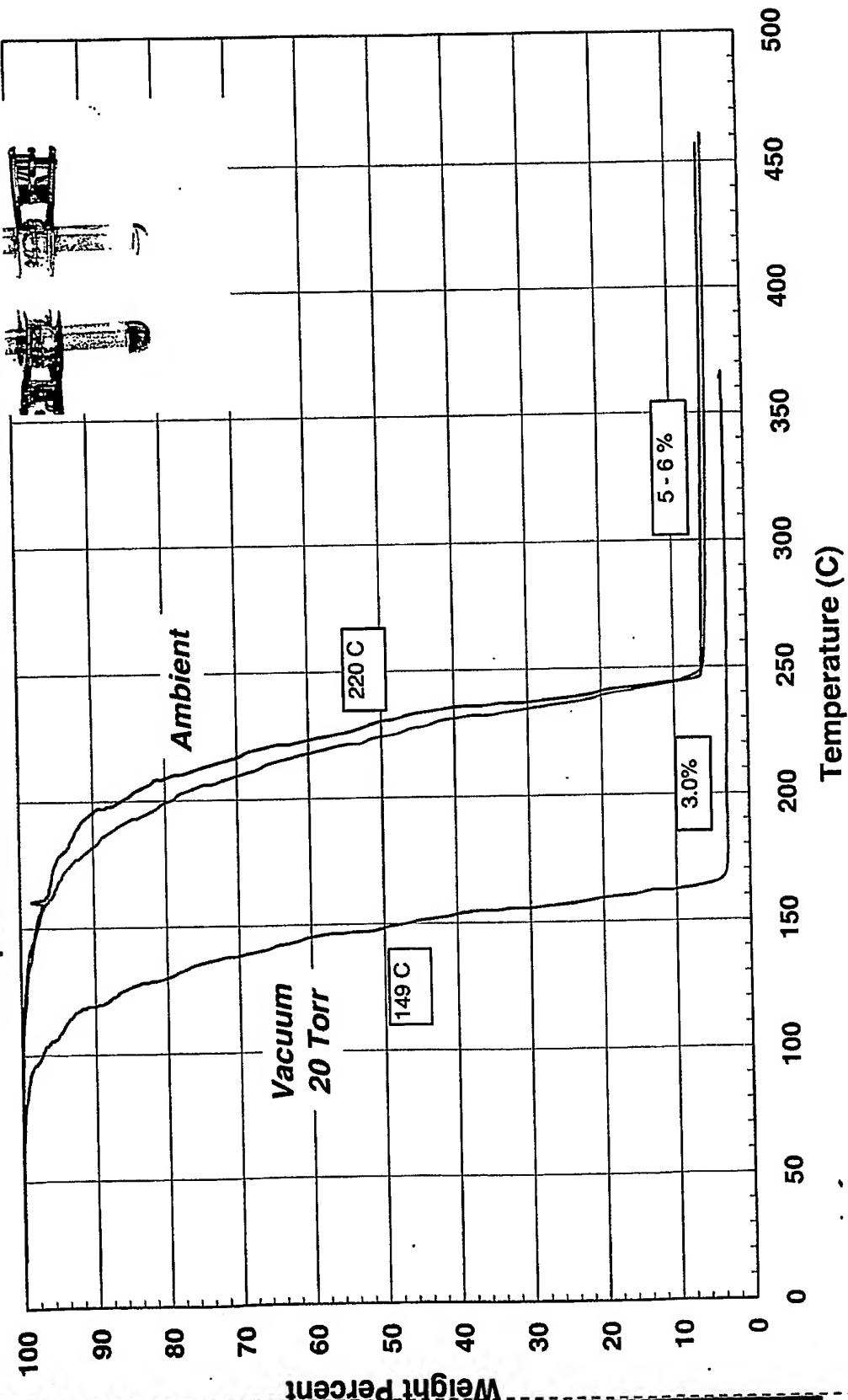


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TGA of Hf(DEA)₄ - 760 Torr vs 20 Torr

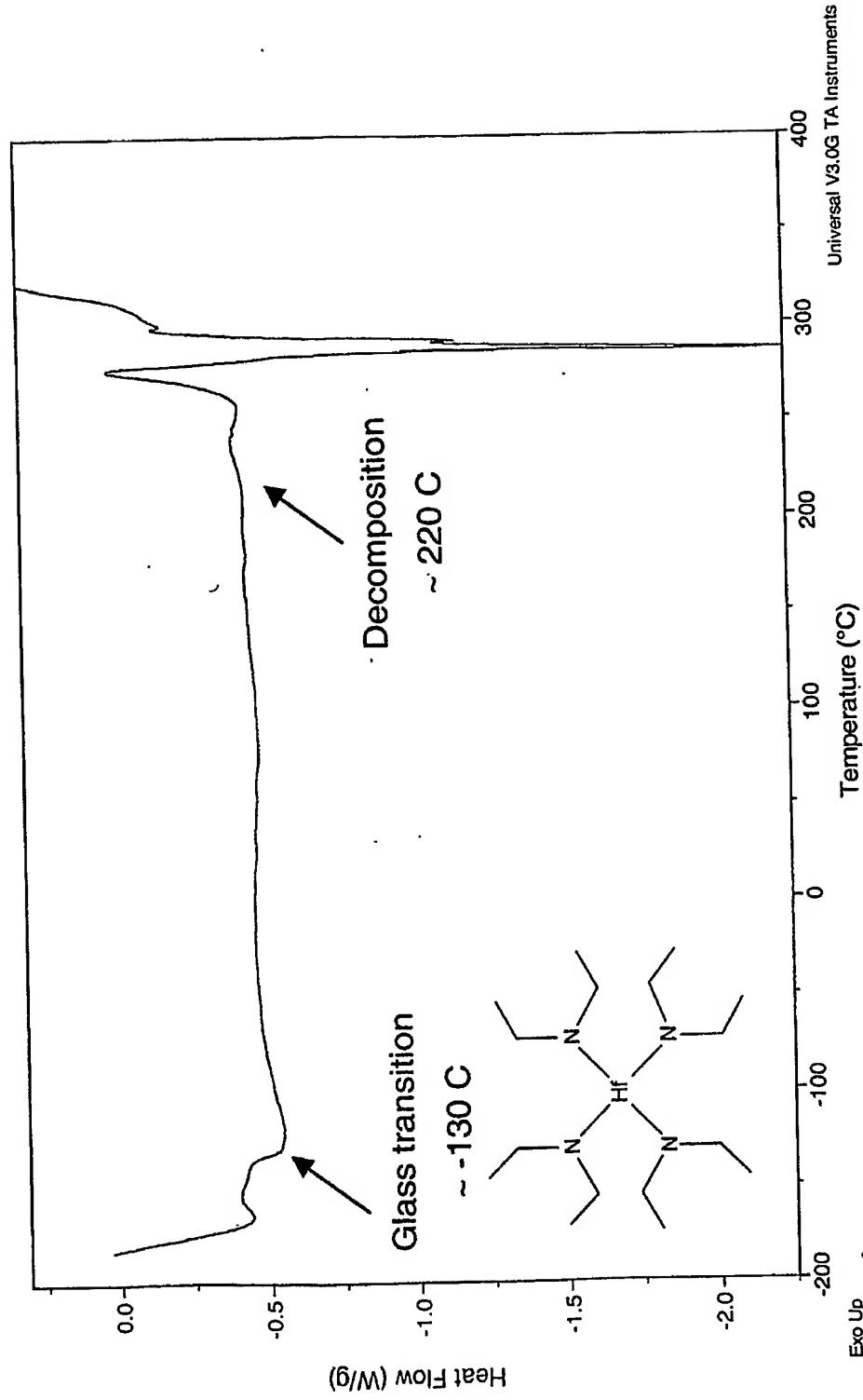


Comparative Analysis of Diethylamino Hafnium



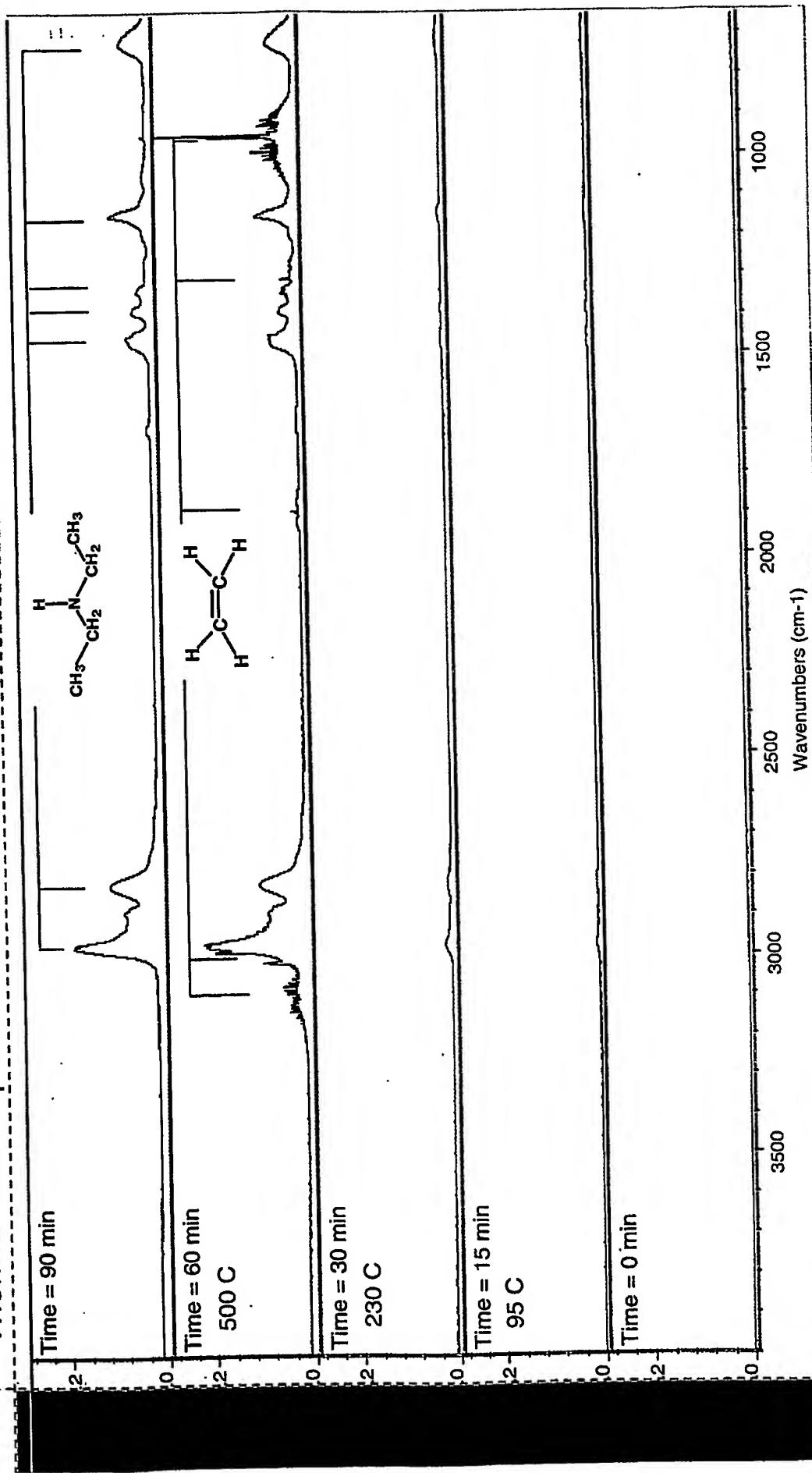
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DSC of Hf(DEA)₄



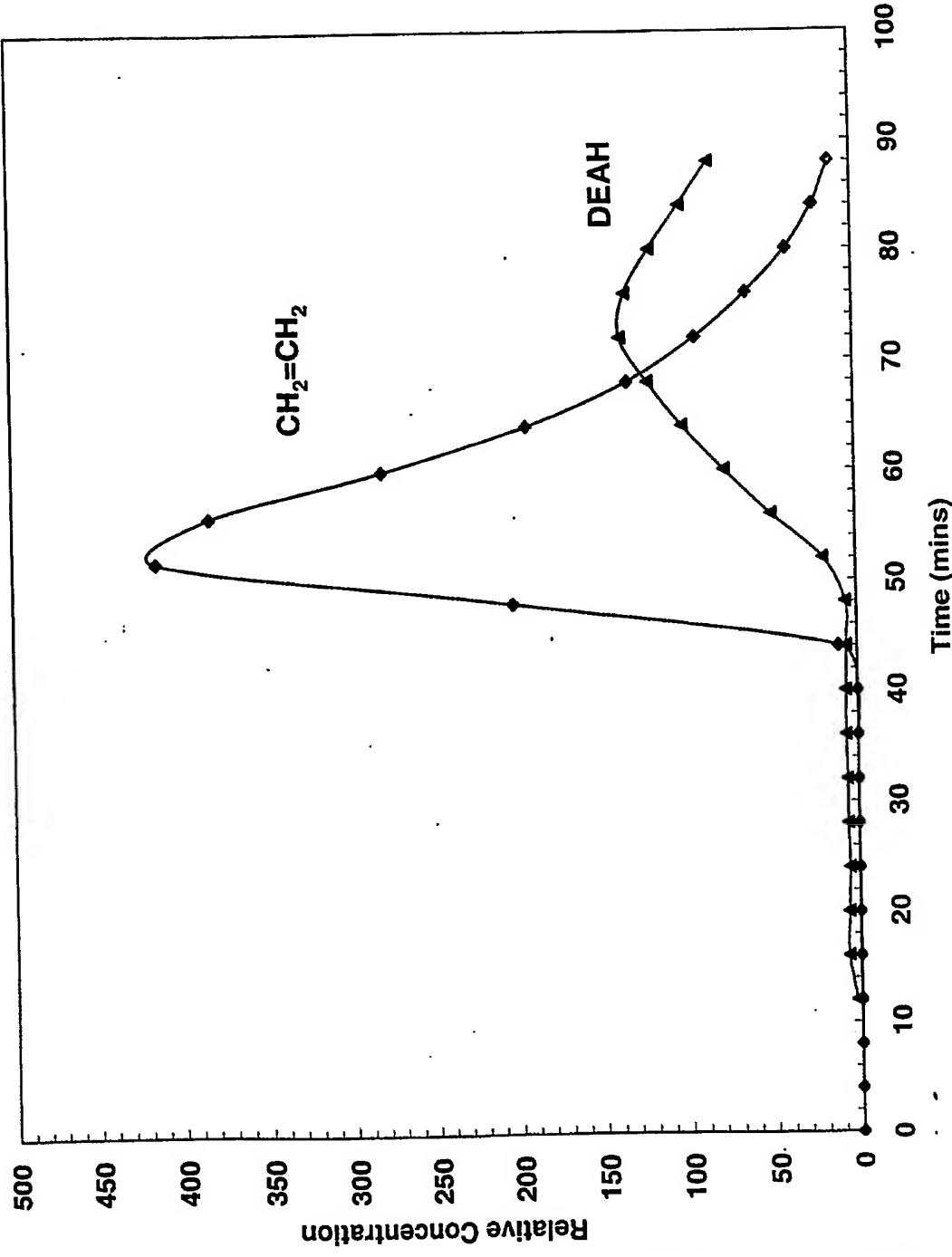
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Time lapsed view of TGA Exhaust at Ambient Pressure Hf(DEA)₄ Thermal Decomposition



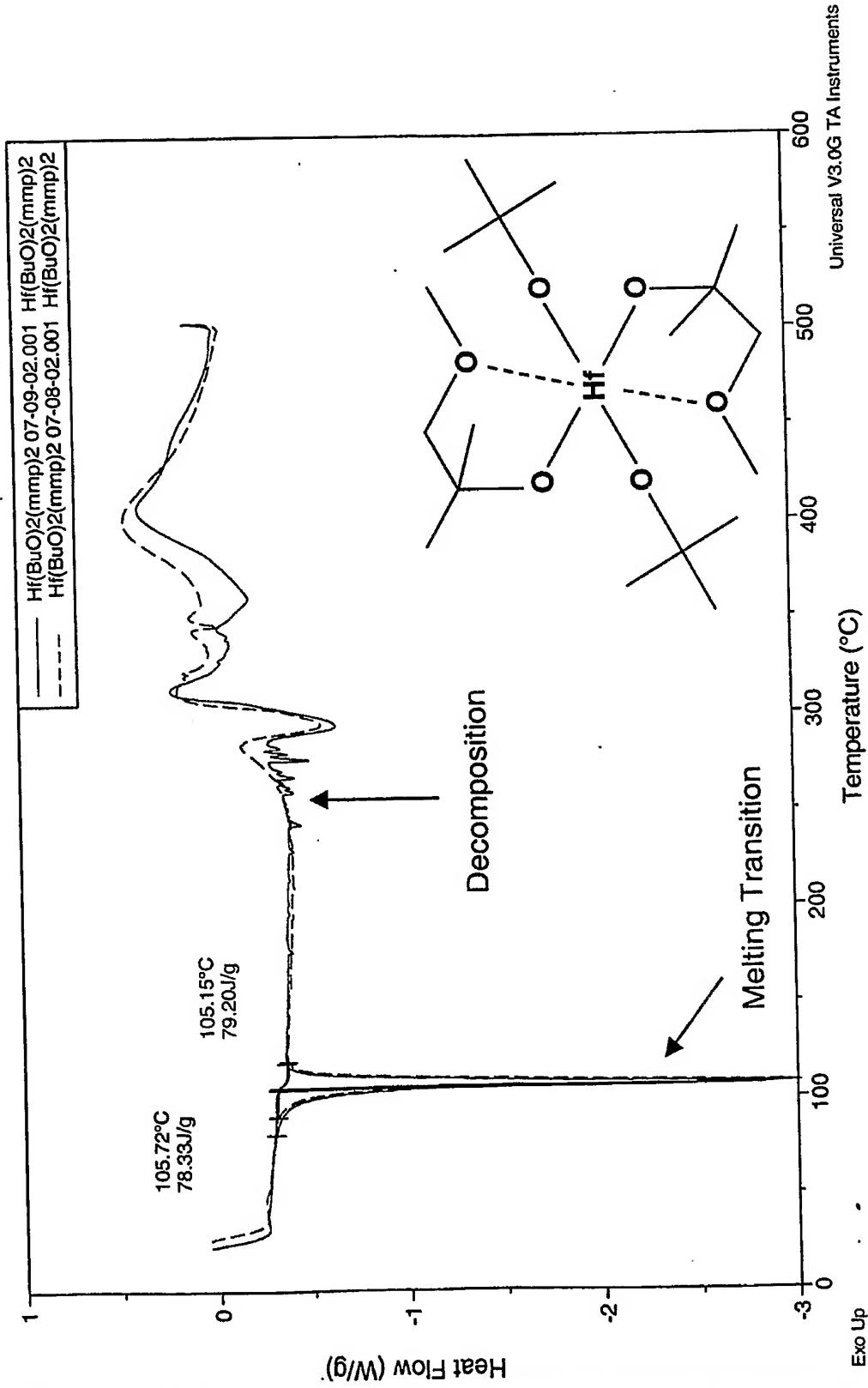
Temporal Profile of TGA Exhaust Products by FTIR

Hf(DEA)₄ Sample



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Hf(t-BuO)₂(mmp)₂



AIR LIQUIDE
Electronics

Universal V3.0G TA Instruments

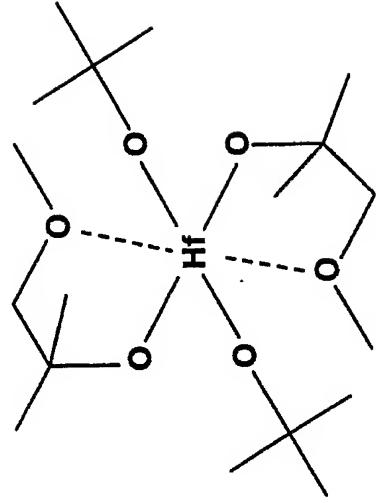
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Information from DSC results on $\text{Hf}(\text{tOBu})_2(\text{mmp})_2$

- Reproducible melting points
 - ✓ Run 1. M.P. = 105.15°C
 - ✓ Run 2. M.P. = 105.72°C
 - ✓ Avg. M.P. = 105.4°C
- Estimated Heat of Fusion
 - ✓ Run 1. $H_f = 79.2 \text{ J/g}$
 - ✓ Run 2. $H_f = 78.3 \text{ J/g}$
 - ✓ Avg. $H_f = 78.8 \text{ J/g}$
- Onset of Decomposition around 250°C

Hf(tOBu)₂(mmp)₂

bis (tertiary butoxy) bis (methoxymethylpropanolate)



Hf(DEA)₄

tetrakis (diethylamino) Hafnium

